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(54) **DETERGENT COMPOSITIONS CONTAINING SOIL RELEASE POLYMERS**

**WASCHMITTEL MIT SCHMUTZLÖSENDE POLYMEREN**

**COMPOSITIONS DETERGENTES CONTENANT DES POLYMERES ANTISALISSURES**

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**EP 0 874 892 B1**

**Description****TECHNICAL AREA**

- 5 **[0001]** The present invention relates to non-bleaching low-pH laundry detergent compositions suitable for washing delicate fabrics, containing certain water-soluble or water-dispersible polyesters exhibiting improved soil release properties.

**BACKGROUND AND PRIOR ART**

- 10 **[0002]** Polyesters of terephthalic and other aromatic dicarboxylic acids having soil release properties are widely disclosed in the art, in particular, the so-called PET/POET (polyethylene terephthalate/polyoxyethylene terephthalate) and PET/PEG (polyethylene terephthalate/polyethylene glycol) polyesters which are disclosed, for example, in US 3 557 039 (ICI), GB 1 467 098 and EP 1305A (Procter & Gamble). Polymers of this type are available commercially, for example, as Permalose, Aquaperle and Milease (Trade Marks) (ICI) and Repel-O-Tex (Trade Mark) SRP3 (Rhône-Poulenc). Other patent publications disclosing soil release polymers which are condensation products of aromatic dicarboxylic acids and dihydric alcohols include EP 185 427A, EP 241 984A, EP 241 985A and EP 272 033A (Procter & Gamble).

- 20 **[0003]** EP 357 280A (Procter & Gamble) discloses sulphonated end-capped linear terephthalate oligomers which are condensation products of a low molecular weight diol, preferably propylene glycol or ethylene glycol, with terephthalic acid.

- 25 **[0004]** The present invention is based on the use, in non-bleaching detergent compositions capable of delivering a low solution pH, of a class of non-end-capped sulphonated polyesters based on dicarboxylic acids and polyols which provide especially effective soil release, especially from polyester fabrics, and which are also effective in reducing soil redeposition in the wash.

**DEFINITION OF THE INVENTION**

- 30 **[0005]** The present invention accordingly provides a non-bleaching laundry detergent composition suitable for washing delicate fabrics, having a 1 wt% aqueous solution pH in demineralised water at 25°C not exceeding 10 and comprising:

- 35 (a) from 2 to 50 wt% of an organic surfactant system comprising one or more anionic, nonionic, cationic, amphoteric or zwitterionic surfactants,

- (b) from 0 to 80 wt% of a builder component comprising one or more inorganic or organic detergency builders,

- (c) a soil release effective amount of a water-soluble or water-dispersible non-end-capped sulphonated polyester comprising monomer units of

- 40 (i) an unsulphonated aromatic diacidic monomer (A),

- (ii) a sulphonated aromatic diacidic monomer (SA)

- 45 (iii) optionally a hydroxylated aromatic or aliphatic diacidic monomer (HA), in an amount replacing up to 50 mole% of (A) and/or (SA),

- (iv) a polyol (P) selected from ethylene glycol, propylene glycol, isopropylene glycol, glycerol, 1,2,4-butanetriol and 1,2,3-butanetriol, and oligomers of these having from 1 to 8 monomer units,

- 50 the polyester having a sulphur content within the range of from 0.5 to 10 wt%;

- (d) optionally other detergent ingredients to 100 wt%.

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DETAILED DESCRIPTION OF THE INVENTIONThe polyesters

5 [0006] The polyesters with which the invention is concerned are defined above. The polyesters and their preparation are disclosed and claimed in WO 95 32997A (Rhône-Poulenc).

[0007] Preferred polyesters have the following features:

- 10 - the unsulphonated diacidic monomer (A) is an aromatic dicarboxylic acid or an anhydride of a lower (C<sub>1</sub>-C<sub>4</sub>) alkyl diester thereof, selected from terephthalic acid, isophthalic acid, 2,6-naphthalene dicarboxylic acid, anhydrides and lower (C<sub>1</sub>-C<sub>4</sub>) alkyl diesters thereof;
- the sulphonated diacidic monomer (SA) is a sulphonated aromatic dicarboxylic acid, anhydride, or lower (C<sub>1</sub>-C<sub>4</sub>) alkyl diester thereof;
- 15 - the mole ratio (A):[(A) + (SA)] is within the range of from 60:100 to 95:100, preferably from 65:100 to 93:100;
- the mole ratio (SA):[(A) + (SA)] is within the range of from 5:100 to 40:100, preferably from 7:100 to 35:100;
- 20 - the hydroxylated monomer (HA), if present, is a hydroxylated aromatic dicarboxylic acid, or anhydride or lower (C<sub>1</sub>-C<sub>4</sub>) dialkyl ester thereof;
- the hydroxylated monomer (HA), if present, does not replace more than 30 mole% of (A) and/or (SA);
- 25 - the quantity of (P) is such that the ratio of OH functional groups of (P) to COOH functional groups (or equivalents) of (A) + (SA) + any (HA) is within the range of from 1.05:1 to 4:1, preferably from 1.1:1 to 3.5:1, and more preferably from 1.8:1 to 3:1;
- the polyester has a number average molecular weight of less than 20 000,
- 30 - the sulphur content is within the range of from 1.2 to 8 wt%;
- the hydroxyl group content is at least 0.2 OH equivalent per kg of polyester.

35 The unsulphonated diacidic monomer (A)

[0008] As previously indicated, the monomer (A) preferably consists of at least one dicarboxylic acid or anhydride chosen from terephthalic, isophthalic and 2,6 naphthalenedicarboxylic acids or anhydrides or their diesters.

40 [0009] Preferably, monomer (A) is present in a quantity corresponding to a molar ratio (A)/[(A) + (SA)] within the range of from 95:100 to 60:100, preferably from 93:100 to 65:100.

[0010] The unsulphonated diacidic monomer (A) preferably consists of 50 to 100 mole%, more preferably 70 to 90 mole%, of terephthalic acid or anhydride or lower alkyl (methyl, ethyl, propyl, isopropyl, butyl) diester, and of 0 to 50 mole%, more preferably from 10 to 30 mole%, of isophthalic acid or anhydride and/or of 2,6-naphthalenedicarboxylic acid or anhydride or lower alkyl (methyl, ethyl, propyl, isopropyl, butyl) diester; the preferred diesters are methyl diesters.

45 [0011] In the unsulphonated diacidic monomer (A) there may additionally be present minor quantities of aromatic diacids other than those mentioned above, such as orthophthalic acid, anthracene, 1,8-naphthalene, 1,4-naphthalene and biphenyl dicarboxylic acids or aliphatic diacids such as adipic, glutaric, succinic, trimethyladipic, pimelic, azelaic, sebacic, suberic, itaconic and maleic acids, etc. in the form of acid, anhydride or lower (methyl, ethyl, propyl, isopropyl, butyl) diesters.

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The sulphonated diacidic monomer (SA)

[0012] Preferably, the sulphonated diacidic monomer (SA) consists of at least one sulphonated aromatic or sulphonated aliphatic dicarboxylic acid or anhydride or lower (C<sub>1</sub>-C<sub>4</sub>) alkyl diester. Aromatic dicarboxylic acids and their derivatives are preferred.

55 [0013] Preferably, monomer (SA) is present in a quantity corresponding to a molar ratio (SA)/[(A) + (SA)] within the range of from 5:100 to 40:100, more preferably from 7:100 to 35:100.

[0014] The sulphonated diacidic monomer (SA) has at least one sulphonic acid group, preferably in the form of an

alkali metal (preferably sodium) sulphonate, and two acidic functional groups or acidic functional group equivalents (that is to say an anhydride functional group or two ester functional groups) attached to one or a number of aromatic rings, when aromatic dicarboxylic acids or anhydrides or their diesters are involved, or to the aliphatic chain when aliphatic dicarboxylic acids or anhydrides or their diesters are involved.

5 [0015] Suitable aromatic sulphonated diacidic monomers include sulphoisophthalic, sulphoterephthalic, sulpho-ortho-phthalic acids or anhydrides, 4-sulpho-2,7-naphthalenedicarboxylic acids or anhydrides, sulpho 4,4'-bis(hydroxycarbonyl) diphenyl sulphones, sulphodiphenyldicarboxylic acids or anhydrides, sulpho 4,4'-bis(hydroxycarbonyl) diphenylmethanes, sulpho-5-phenoxyisophthalic acids or anhydrides or their lower (methyl, ethyl, propyl, isopropyl, butyl) diesters.

10 [0016] Suitable aliphatic sulphonated diacidic monomers (SA) include sulphosuccinic acids or anhydrides or their lower alkyl (methyl, ethyl, propyl, isopropyl, butyl) diesters.

[0017] The most preferred sulphonated diacidic monomer (SA) is sulphoisophthalic acid in acid, anhydride or diester (preferably dimethyl ester) form, very particularly dimethyl 5-sodiooxsulphonylisophthalate.

#### 15 The hydroxylated diacidic monomer (HA)

[0018] The hydroxylated diacidic monomer (HA), which is optionally present and can replace up to 50 mole%, preferably up to 30 mole%, of (A) and/or (SA), consists of least one hydroxylated aromatic or aliphatic dicarboxylic acid or anhydride or a lower (C1-C4) alkyl diester thereof.

20 [0019] The hydroxylated diacidic monomer (HA) has at least one hydroxyl group attached to one or a number of aromatic rings when it is an aromatic monomer or to the aliphatic chain when it is an aliphatic monomer. Aromatic monomers are preferred.

[0020] Suitable hydroxylated diacidic monomers (HA) include 5-hydroxyisophthalic, 4-hydroxyisophthalic, 4-hydroxyphthalic, 2-hydroxymethylsuccinic, hydroxymethylglutaric and hydroxyglutaric acids, in acid, anhydride or lower alkyl diester form.

#### The polyol (P)

30 [0021] The polyol (P) may be a oligomer comprising up to 8 monomer units, preferably up to 6 and more preferably up to 4 monomer units, but is most preferably a monomer. The polyol is selected from ethylene glycol, propylene glycol, glycerol, 1,2,4-butanetriol, 1,2,3-butanetriol and combinations of these, and their lower (2 to 8, preferably 2 to 6, more preferably 2 to 4) oligomers.

[0022] Preferably, the polyol (P) is present in a quantity corresponding to a ratio of the number of OH functional groups of the polyol (P) to the number of COOH functional groups or functional group equivalents of the total diacidic monomer (A) + (SA) + (HA) within the range of from 1.05:1 to 4:1, preferably from 1.1:1 to 3.5:1 and more preferably from 1.8:1 to 3:1.

[0023] The preferred polyols (P) are ethylene glycol and glycerol, ethylene glycol being especially preferred.

40 [0024] Preferably, the sulphonated diacidic monomer (SA) consists of at least one sulphonated aromatic dicarboxylic acid or anhydride or of a mixture of sulphonated aromatic acids or anhydrides and of sulphonated aliphatic acids or anhydrides or their diesters when the polyol (P) does not contain any polyol other than a glycol or when the hydroxylated diacidic monomer (HA) is absent.

#### Molecular weight

45 [0025] Preferably, the polyester used in accordance with the invention has a number average molecular weight not exceeding 20 000, and preferably not exceeding 15 000.

[0026] The molecular weight may be much lower than these limits. Polyesters having molecular weights below 1000, for example, 500-1000, have proved highly effective.

50 [0027] Number average molecular weight may be measured by gel permeation chromatography, for example, in dimethylacetamide containing  $10^{-2}$  N of LiBr, at 25°C, or in tetrahydrofuran. The results are expressed as polystyrene equivalents.

#### Hydroxyl functional group content

55 [0028] Preferably, the hydroxyl functional group content of the polyester, expressed as OH equivalent/kg of polyester, is at least 0.2. The hydroxyl functional group content may be estimated from proton NMR, the measurement being carried out in dimethyl sulphoxide.

[0029] The elementary unit considered in the definition of the mole of monomer (A), (SA) or (HA) is the COOH

functional group in the case of the diacids or the COOH functional group equivalent in the case of the anhydrides or of the diesters.

#### Especially preferred polyesters

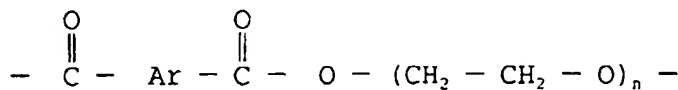
**[0030]** An especially preferred polyester is obtainable from the following monomers:

- terephthalic acid (A1) in lower alkyl (preferably methyl) diester form;
- optionally isophthalic acid (A2) in acid or anhydride form;
- optionally a hydroxylated terephthalic or isophthalic acid (HA) in acid or anhydride form;

the mole ratio (A1): [(A1) + (A2)] or (A1):[A1 + HA] or (A1): [(A1) + (A2) + (HA)] being within the range of from 50:100 to 100:100, preferably from 70:100 to 90:100;

- sulphoisophthalic acid (SA), preferably in lower alkyl, preferably methyl, diester form; and
- monoethylene glycol and/or glycerol (P).

**[0031]** Preferred polyesters in accordance with the invention, based on terephthalic acid, isophthalic acid, sulphoisophthalic acid and monoethylene glycol, may be described as having backbone units of the following formula:

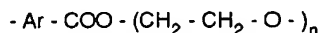


where Ar = terephthalic, isophthalic or sulphoisophthalic, and  $n$  represents 1, 2, 3 or 4. Typical mole percentages for the different values of  $n$  are as follows:

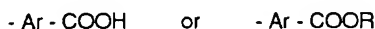
$n = 1$	58.7
$n = 2$	30.5
$n = 3$	8.8
$n = 4$	1.9,

only trace quantities, if any, of polyethylene oxide units in which  $n$  is greater than four being present.

**[0032]** The majority of endgroups are of the formula



wherein  $n$  is 1, 2, 3 or 4, a minority being of the formulae



wherein R is a lower alkyl group, preferably methyl.

**[0033]** These polyesters, unlike many disclosed in the prior art, are not end-capped with hydrocarbon or sulphonated capping groups.

#### Preparation of the polyesters

**[0034]** The polyesters may be prepared by the usual esterification and/or transesterification and polycondensation processes, for example, by esterification and/or transesterification in the presence of a catalyst of the polyol P with the

various diacidic monomers (in acid, anhydride or diester form), and polycondensation of the polyol esters at reduced pressure in the presence of a polycondensation catalyst.

[0035] A preferred process for the preparation of the polyesters is disclosed and claimed in WO 95 32997A (Rhône-Poulenc).

#### Detergent compositions

[0036] The polyesters are suitably incorporated into detergent compositions in amounts of from 0.01 to 10 wt%, preferably from 0.1 to 5 wt% and more preferably from 0.25 to 3 wt%.

[0037] The detergent compositions of the invention also contain, as essential ingredients, one or more detergent-active compounds (surfactants), and may also contain one or more detergency builders; they may also optionally contain other active ingredients to enhance performance and properties.

#### Surfactant system

[0038] The detergent-active compounds (surfactants) may be chosen from soap and non-soap anionic, cationic, nonionic, amphoteric and zwitterionic detergent-active compounds, and mixtures thereof. Many suitable detergent-active compounds are available and are fully described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch. The preferred detergent-active compounds that can be used are soaps and synthetic non-soap anionic and nonionic compounds. The total amount of surfactant present ranges from 2 to 50 wt%, preferably from 5 to 40 wt%.

[0039] Anionic surfactants are well-known to those skilled in the art. Examples include alkylbenzene sulphonates, particularly linear alkylbenzene sulphonates having an alkyl chain length of C<sub>8</sub>-C<sub>15</sub>; primary and secondary alkylsulphates, particularly C<sub>8</sub>-C<sub>15</sub> primary alkyl sulphates; alkyl ether sulphates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates. Sodium salts are generally preferred.

[0040] The polyesters of the present invention are especially suitable for use in compositions containing anionic sulphonate and sulphate type surfactants, for example, primary alkyl sulphates, alkyl ether sulphates, alkylbenzene sulphonates, and mixtures of these.

[0041] Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C<sub>8</sub>-C<sub>20</sub> aliphatic alcohols ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the C<sub>10</sub>-C<sub>15</sub> primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkylpolyglycosides, glycerol monoethers, and polyhydroxyamides (glucamide).

[0042] Especially preferred are ethoxylated nonionic surfactants, alkylpolyglycosides, and mixtures of these.

[0043] As well as the non-soap surfactants listed above, detergent compositions of the invention may also advantageously contain fatty acid soap.

#### Detergency builder system

[0044] The detergent compositions of the invention will generally also contain one or more detergency builders. The total amount of detergency builder in the compositions will suitably range from 5 to 80 wt%, preferably from 10 to 60 wt%.

[0045] Inorganic builders that may be present include sodium carbonate, if desired in combination with a crystallisation seed for calcium carbonate, as disclosed in GB 1 437 950 (Unilever); crystalline and amorphous aluminosilicates, for example, zeolites as disclosed in GB 1 473 201 (Henkel), amorphous aluminosilicates as disclosed in GB 1 473 202 (Henkel) and mixed crystalline/amorphous aluminosilicates as disclosed in GB 1 470 250 (Procter & Gamble); and layered silicates as disclosed in EP 164 514B (Hoechst). Inorganic phosphate builders, for example, sodium orthophosphate, pyrophosphate and tripolyphosphate, may also be present.

[0046] According to one preferred embodiment of the invention, the detergent compositions of the invention preferably contain an alkali metal, preferably sodium, aluminosilicate builder. Sodium aluminosilicates may generally be incorporated in amounts of from 10 to 70% by weight (anhydrous basis), preferably from 25 to 50 wt%.

[0047] The zeolite may be the commercially available zeolite 4A now widely used in laundry detergent powders. Other zeolites that may be used include zeolites X and Y. Alternatively, and preferably, the zeolite builder incorporated in the compositions of the invention is maximum aluminium zeolite P (zeolite MAP) as described and claimed in EP 384 070B (Unilever). Zeolite MAP is defined as an alkali metal aluminosilicate of the zeolite P type having a silicon to aluminium ratio not exceeding 1.33.

[0048] Especially preferred is zeolite MAP having a silicon to aluminium ratio not exceeding 1.07, more preferably about 1.00. The calcium binding capacity of zeolite MAP is generally at least 150 mg CaO per g of anhydrous material.

[0049] According to another preferred embodiment of the invention, the builder system comprises at least 5 wt%,

and preferably at least 10 wt%, of sodium tripolyphosphate (the percentages being based on the detergent composition).

[0050] Sodium tripolyphosphate is suitably present in an amount of from 5 to 50 wt%; if sole builder, it is suitably present in an amount of from 20 to 50 wt%.

5 [0051] Sodium tripolyphosphate may also advantageously be used in combination with other builders, most preferably, sodium carbonate, sodium orthophosphate, sodium pyrophosphate, or sodium aluminosilicate (zeolite). One preferred mixed builder system comprises at least 5 wt% sodium tripolyphosphate in combination with at least 10 wt% of zeolite A.

10 [0052] Organic builders that may be present include polycarboxylate polymers such as polyacrylates, acrylic/maleic copolymers, and acrylic phosphinates; monomeric polycarboxylates such as citrates, gluconates, oxydisuccinates, glycerol mono-, di- and trisuccinates, carboxymethyloxysuccinates, carboxymethyloxymalonates, dipicolinates, hydroxyethyliminodiacetates, alkyl- and alkenylmalonates and succinates; and sulphonated fatty acid salts. This list is not intended to be exhaustive.

#### 15 Solution pH

[0053] The compositions of the invention, which are non-bleaching formulations especially suitable for washing delicate fabrics, produce a wash liquor of low pH. The 1 wt% solution pH at 25°C in demineralised water of the compositions of the invention does not exceed 10, and is preferably within the range of from 9.5 to 10.

20

#### Other care ingredients

[0054] The compositions of the invention may advantageously possess one or more of the following characteristics:

- 25 - absence, or an extremely low level, not more than 0.1 wt%, of fluorescer;
- presence of a polycarboxylate polymer, for example, an acrylic/maleic copolymer such as Sokalan (Trade Mark) CP5 ex BASF;
- 30 - presence of a polymer effective to inhibit dye transfer, for example, polyvinyl pyrrolidone;
- presence of a heavy metal sequestrant, for example, aminomethylenephosphonic acids and salts such as ethylenediamine tetramethylene phosphonate (EDTMP) and its salts, and diethylenetriamine pentamethylene phosphonate (DETPMP) and its salts.
- 35 - presence of at least two enzymes.

[0055] Suitable enzymes include the proteases, amylases, cellulases and lipases usable for incorporation in detergent compositions.

40 [0056] Preferred proteolytic enzymes (proteases) are normally solid, catalytically active protein materials which degrade or alter protein types of stains when present as in fabric stains in a hydrolysis reaction. They may be of any suitable origin, such as vegetable, animal, bacterial or yeast origin.

[0057] Proteolytic enzymes or proteases of various qualities and origins and having activity in various pH ranges of from 4-12 are available and can be used in the present invention. Examples of suitable proteolytic enzymes are the subtilisins, which are obtained from particular strains of *B. subtilis* and *B. licheniformis*, such as the commercially available subtilisins Maxatase (Trade Mark), as supplied by Gist-Brocades N.V., Delft, Holland, and Alcalase (Trade Mark), as supplied by Novo Industri A/S, Copenhagen, Denmark.

[0058] Also suitable is a protease obtained from a strain of *Bacillus* having maximum activity throughout the pH range of 8-12, being commercially available, e.g. from Novo Industri A/S under the registered trade-names Esperase (Trade Mark) and Savinase (Trade Mark). The preparation of these and analogous enzymes is described in GB 1 243 785. Other commercial proteases are Kazusase (Trade Mark) (obtainable from Showa-Denko of Japan), Optimase (Trade Mark) (from Miles Kali-Chemie, Hannover, West Germany), and Superase (Trade Mark) (obtainable from Pfizer of U.S.A.).

55 [0059] Proteases having isoelectric points below 10 include Alcalase, Maxatase, Optimase and Primase (all Trade Marks). Proteases having isoelectric points of 10 or above include Savinase, Maxacal, Purafect, Opticlean and Esperase (all Trade Marks):

[0060] Detergency enzymes are commonly employed in granular form in amounts of from 0.01 to 5.0 wt%.

[0061] Preferably the compositions of the invention contain at least two enzymes, which are preferably a protease

and a lipase. Optionally an amylase and/or a cellulase may also be present.

[0062] In particulate compositions of the invention, the enzymes are suitably present in granular form.

[0063] The compositions may then suitably contain protease granules in an amount of from 0.1 to 5 wt% and lipase granules in an amount of from 0.01 to 1 wt%, or protease/lipase granules in an amount of from 0.1 to 5 wt%; and optionally amylase granules in an amount of from 0.01 to 1 wt%, and/or cellulase granules in an amount of from 0.01 to 1 wt%.

[0064] Other materials that may be present in detergent compositions of the invention include inorganic salts such as sodium carbonate, sodium sulphate or sodium silicate; antiredeposition agents such as cellulosic polymers; inorganic salts such as sodium sulphate; lather control agents or lather boosters as appropriate; dyes; coloured speckles; perfumes; foam controllers; and fabric softening compounds. This list is not intended to be exhaustive.

[0065] Detergent compositions of the invention may be of any suitable physical form, for example, powders or granules, liquids, gels and solid bars.

[0066] Detergent compositions of the invention may be prepared by any suitable method. Particulate detergent compositions are suitably prepared by spray-drying a slurry of compatible heat-insensitive ingredients, and then spraying on or postdosing those ingredients unsuitable for processing via the slurry. The skilled detergent formulator will have no difficulty in deciding which ingredients should be included in the slurry and which should not.

[0067] Particulate detergent compositions of the invention preferably have a bulk density of at least 400 g/l, more preferably at least 500 g/l.

[0068] Especially preferred compositions have bulk densities of at least 650 g/litre, more preferably at least 700 g/litre.

[0069] Such powders may be prepared either by post-tower densification of spray-dried powder, or by wholly non-tower methods such as dry mixing and granulation; in both cases a high-speed mixer/granulator may advantageously be used. Processes using high-speed mixer/granulators are disclosed, for example, in EP 340 013A, EP 367 339A, EP 390 251A and EP 420 317A (Unilever).

## 25 EXAMPLES

[0070] The invention is further illustrated by the following non-limiting Examples, in which parts and percentages are by weight unless otherwise stated. Throughout the Examples \* denotes a Trade Mark.

## 30 Polymers

[0071] The polymer in accordance with the invention used (Polymer 1) was a water-soluble sulphonated polyester of terephthalic acid, isophthalic acid, sulphisophthalic acid and ethylene glycol having the following approximate composition:

- diacidic monomer comprising approximately 77 mole% terephthalate, 3.7 mole% isophthalate, 18.2 mole% sulphisophthalate;
- ratio of OH groups ex ethylene glycol to COOH groups ex diacid monomers approximately 1.22;
- number average molecular weight, by GPC in tetrahydrofuran at 25°C with calibration against polystyrene standards, 534; weight average molecular weight 1667;
- sulphur content 2.4 wt%;
- hydroxyl group content approximately 1.4-1.5 per kg polyester.

[0072] For comparative purposes, the following commercially available polymers were used:

50 Polymer A: Sokalan (Trade Mark) HP22 ex BASF, a graft copolymer of polyethylene glycol and polyvinyl acetate.

Polymer B: Repel-O-Tex (Trade Mark) ex Rhône-Poulenc, a PET/POET polymer, used in the form of a granule (50% wt% polymer, 50 wt% sodium sulphate).

## 55 EXAMPLE 1

[0073] Phosphate-built particulate detergent compositions were prepared to the following general formulation, using spray-drying and postdosing techniques:



Na linear alkylbenzene sulphonate	25.00
Zeolite	1.17
Sodium tripolyphosphate	21.68
Sodium silicate	5.00
Calcium carbonate	10.00
Sodium sulphate	21.24
Sodium carboxymethylcellulose	0.70
Fluorescer	0.01
Acrylic/maleic copolymer (Sokalan* CP5)	1.80
Perfume	0.25
Protease (Savinase* 6T)	0.20
Lipase (Lipolase* 100T)	0.05
Amylase (Termamyl* 60T)	0.08
Antifoam (silicone oil/silica)	0.01
Soil release polymer	see below
Moisture and impurities	to 100.00

[0074] The formulations had a bulk density of 420-440 g/litre and a 1 wt% aqueous solution pH in demineralised water at 25°C of 9.7-9.8.

[0075] Soil release and detergency on knitted polyester test cloths stained with Oilsol Blue dye/olive oil, were assessed in the tergotometer at two different product dosages, using the following wash regimes:

	3.8 g/l	1.3 g/l
Water hardness	25:3 Ca:Mg	15:3 Ca:Mg
pH	8.45	8.22
Temperature	28°C	
Soak/wash time	30 min soak/10 min wash	
Prewashes	5	
Replicates	2	

[0076] Detergency was assessed by measuring reflectance before and after washing using Micromatch (Trade Mark) apparatus. The differences ( $\Delta R_{580^*}$ ) are shown in the following Table:

Polymer	%	3.8 g/l	1.3 g/l
None	0	32.68	22.94
Polymer 1	0.5	57.29	63.02
Polymer A	1.0	50.63	27.96
Polymer B	0.5	52.05	50.41

[0077] Stain removal was also assessed visually by an experienced panel of five people. The results, expressed on a scale of 1 (heavy staining, initial stain) to 10 (complete removal), were as follows:

Polymer	%	3.8 g/l	1.3 g/l
Initial	-	1	1
None	0	3	3
Polymer 1	0.5	10	10
Polymer A	1.0	6	4
Polymer B	0.5	8	8

**EXAMPLE 2**

[0078] Further phosphate-built particulate detergent compositions were prepared to the following general formula-  
tion, using spray-drying and postdosing techniques:

Na linear alkylbenzene sulphonate	25.00
Sodium tripolyphosphate	22.50
Sodium silicate	5.00
Sodium sulphate	28.90
Sodium carboxymethylcellulose	0.70
Acrylic/maleic copolymer (Sokalan* CP5)	2.00
Sodium carbonate	2.00
Fluorescer speckles	1.00
Citric acid (anhydrous)	3.00
Protease (Opticlean* M375)	0.784
Lipase (Lipolase* 100T)	0.253
Antifoam (silicone oil/silica)	0.04
Perfume	0.33
Soil release polymer	see below
Moisture and impurities	to 100.00

[0079] The formulations had a bulk density of 370-430 g/litre and a 1 wt% aqueous solution pH in demineralised water at 25°C of 9.7-9.8.

[0080] Detergency was assessed, as in Example 1, by measuring reflectance before and after washing using Micro-match (Trade Mark) apparatus. The differences ( $\Delta R$  580\*) are shown in the following Table:

Polymer	%	3.8 g/l	1.3 g/l
None	0	30.34	38.56
Polymer 1	0.25	57.84	60.67
Polymer A	1.0	53.23	59.48
Polymer B	0.25	53.71	61.77
Polymer B	0.35	54.50	58.53

[0081] Soil release properties were also assessed at a product dosage of 1.3 g/l, by measuring reflectance after a first wash and again after a second wash. The wash regime in the tergotometer was as follows:

Test cloth	Knitted polyester
Stain	Oilsol Violet/olive oil
Water hardness	21:6 Ca:Mg
Temperature	28°C
Prewashes	none
Soak/wash time	30 min soak/10 min wash
Rinse time	2 x 2 min

**Results**

[0082]

Polymer	%	R 580*			
		Wash 1	Wash 2	Difference	
None	0	42.30	44.49	2.19 )	2.70
		43.34	46.55	3.21 )	

(continued)

Polymer	%	R 580*			
		Wash 1	Wash 2	Difference	
1	1.0	46.75	58.31	11.56 )	12.99
		56.05	70.47	14.42 )	
B	1.0	50.45	60.52	10.07 )	10.12
		45.58	55.75	10.17 )	

**EXAMPLE 3**

[0083] An example of a phosphate-built non-bleaching high bulk density particulate detergent composition containing soil release polymer of the invention is as follows:

Na LAS <sup>1</sup>	28.66
Na PAS <sup>2</sup>	2.88
Nonionic 9EO	-
Zeolite	18.84
Na tripolyphosphate	29.69
Na carbonate	-
Na bicarbonate	6.26
Na silicate	-
SCMC	0.78
Fluorescer	0.01
Copolymer (Sokalan* CP5)	1.93
Protease (Savinase* 6T)	0.32
Lipase (Lipolase* 100T)	0.08
Amylase (Termamyl* 60T)	0.14
Soil release polymer	0.50
Perfume	0.40
Moisture and impurities	to 100 wt%
Bulk density (g/litre)	780-820

<sup>1</sup>Sodium linear alkylbenzene sulphonate

<sup>2</sup>Sodium primary alcohol sulphate

[0084] The composition is of low solution pH (9.7-9.8) and is especially suitable for washing delicate fabrics.

**EXAMPLE 4**

[0085] A further example of a high bulk density non-bleaching phosphate-built powder of low solution pH in accordance with the invention, suitable for washing delicate fabrics, is as follows:

Na LAS	6.50
Nonionic 6/7EO	4.00
Soap	4.30
Na tripolyphosphate	29.17
Na silicate	10.00
SCMC	0.43
Polyvinyl pyrrolidone	0.95
Na sulphate	17.00
Na carbonate (heavy)	6.00

(continued)

Ammonium sulphate	2.00
Citric acid	2.25
Na metasilicate	2.00
Amorphous aluminosilicate	1.12
Protease (Savinase* 6T)	0.20
Lipase (Lipolase* 100T)	0.05
Amylase (Termamyl* 60T)	0.25
Cellulase (Celluzyme* 0.7T)	0.40
Soil release polymer	0.55
Perfume	0.40
Moisture and impurities	to 100.00

[0086] The bulk density of this formulation is 700 g/litre and the 1 wt% aqueous solution pH in demineralised water is 9.7-9.8.

## Claims

1. A non-bleaching laundry detergent composition suitable for washing delicate fabrics, comprising:

(a) from 2 to 50 wt% of an organic surfactant system comprising one or more anionic, nonionic, cationic, amphoteric or zwitterionic surfactants,

(b) from 0 to 80 wt% of a builder component comprising one or more inorganic or organic detergency builders,

(c) a soil release effective amount of a water-soluble or water-dispersible soil release polymer,

(d) optionally other detergent ingredients to 100 wt%,

characterised in that the composition has a 1 wt% aqueous solution pH in demineralised water at 25°C not exceeding 10, and the soil release polymer comprises a water-soluble or water-dispersible non-end-capped sulphonated polyester comprising monomer units of

(i) an unsulphonated aromatic diacidic monomer (A),

(ii) a sulphonated aromatic diacidic monomer (SA)

(iii) optionally a hydroxylated aromatic or aliphatic diacidic monomer (HA), in an amount replacing up to 50 mole% of (A) and/or (SA),

(iv) a polyol (P) selected from ethylene glycol, propylene glycol, isopropylene glycol, glycerol, 1,2,4-butanetriol and 1,2,3-butanetriol, and oligomers of these having from 1 to 8 monomer units,

the polyester having a sulphur content within the range of from 0.5 to 10 wt%.

2. A detergent composition as claimed in claim 1, characterised in that it comprises from 0.01 to 10 wt% of the polyester (c).

3. A detergent composition as claimed in claim 2, characterised in that it comprises from 0.1 to 5 wt% of the polyester (c).

4. A detergent composition as claimed in any preceding claim, characterised in that the 1 wt% aqueous solution pH in demineralised water at 25°C is within the range of from 9.5 to 10.

5. A detergent composition as claimed in any preceding claim, characterised in that the organic surfactant system

comprises primary alkyl sulphate and/or alkyl ether sulphate and/or alkylbenzene sulphonate optionally in combination with a nonionic surfactant.

- 5 6. A detergent composition as claimed in any preceding claim, characterised in that it comprises no more than 0.1 wt% of fluorescer.
7. A detergent composition as claimed in any preceding claim, characterised in that it further comprises a polycarboxylate polymer selected from polyacrylates and acrylic/maleic copolymers.
- 10 8. A detergent composition as claimed in any preceding claim, characterised in that it further comprises a polymer capable of inhibiting dye transfer.
9. A detergent composition as claimed in claim 8, characterised in that the polymer capable of inhibiting dye transfer comprises polyvinyl pyrrolidone.
- 15 10. A detergent composition as claimed in any preceding claim, characterised in that it comprises an enzyme system comprising at least two different enzymes selected from proteases, lipases, amylases and cellulases.
- 20 11. A detergent composition as claimed in any preceding claim, characterised in that it further comprises a sequestrant for di- and polyvalent metals.
12. A detergent composition as claimed in any preceding claim, which is particulate.

## 25 Patentansprüche

1. Eine nicht-bleichende Wäscherei-Waschmittelzusammensetzung, geeignet für das Waschen von empfindlichen Geweben, umfassend:
  - 30 (a) Von 2 bis 50 Gew.-% eines organischen Tensid-Systems, enthaltend ein oder mehrere anionische, nicht-ionische, kationische, amphotere oder zwitterionische Tenside,
  - (b) von 0 bis 80 Gew.-% einer Waschmittelkomponente, enthaltend einen oder mehrere anorganische oder organische Waschkraftbuilder,
  - 35 (c) eine schmutzlösende wirksame Menge eines Wasser-löslichen oder Wasser-dispergierbaren schmutzlösenden Polymeren,
  - (d) wahlweise andere Waschmittelbestandteile bis 100 Gew.-%, dadurch gekennzeichnet, daß die Zusammensetzung einen Igewichtsprozentigen wässrigen Lösungs-pH in entmineralisiertem Wasser bei 25°C, nicht übersteigend 10, hat, und das schmutzlösende Polymere einen Wasser-löslichen oder Wasser-dispergierbaren nichtendständig abgeschlossenen sulfonierten Polyester umfaßt, enthaltend Monomer-Einheiten von
    - 40 (i) einem nicht-sulfonierten aromatischen zweisäurigen Monomeren (A),
    - (ii) einem sulfonierten aromatischen zweisäurigen Monomeren (SA),
    - (iii) gegebenenfalls einem hydroxylierten aromatischen oder aliphatischen zweisäurigen Monomeren (HA), in einer Menge, ersetzend bis zu 50 Mol-% von (A) und/oder (SA),
    - 45 (iv) einem Polyol (P), ausgewählt aus Ethylenglykol, Propylenglykol, Isopropylenglykol, Glycerin, 1,2,4-Butantriol und 1,2,3-Butantriol, und Oligomere von diesen mit von 1 bis 8 Monomer-Einheiten, wobei die Polyester einen Schwefelgehalt innerhalb des Bereiches von 0,5 bis 10 Gew.-% haben.
2. Eine Waschmittel-Zusammensetzung, wie in Anspruch 1 beansprucht, dadurch gekennzeichnet, daß sie von 0,01 bis 10 Gew.-% des Polyesters (c) enthält.
3. Eine Waschmittel-Zusammensetzung wie in Anspruch 2 beansprucht, dadurch gekennzeichnet, daß sie von 0,1 bis 5 Gew.-% des Polyesters (c) enthält.
- 55 4. Eine Waschmittel-Zusammensetzung wie in irgendeinem vorstehenden Anspruch beansprucht, dadurch gekennzeichnet, daß der Igewichtsprozentige wässrige Lösungs-pH-Wert in entmineralisiertem Wasser bei 25°C innerhalb des Bereiches von 9,5 bis 10 liegt.

5. Eine Waschmittel-Zusammensetzung wie in irgendeinem vorstehenden Anspruch beansprucht, dadurch gekennzeichnet, daß das organische Tensid-System primäres Alkylsulfat und/oder Alkylethersulfat und/oder Alkylbenzolsulfonat, wahlweise in Kombination mit einem nichtionischen Tensid, umfaßt.
- 5 6. Eine Waschmittel-Zusammensetzung wie in irgendeinem vorstehenden Anspruch beansprucht, dadurch gekennzeichnet, daß sie nicht mehr als 0,1 Gew.% Fluoreszenzmittel umfaßt.
7. Eine Waschmittel-Zusammensetzung wie in irgendeinem vorstehenden Anspruch beansprucht, dadurch gekennzeichnet, daß sie ferner ein Polycarboxylat-Polymeres enthält, ausgewählt aus Polyacrylaten und Acryl-/Malein-Copolymeren.
- 10 8. Eine Waschmittel-Zusammensetzung wie in irgendeinem vorstehenden Anspruch beansprucht, dadurch gekennzeichnet, daß sie ferner ein Polymeres enthält, fähig der Inhibierung der Farbstoff-Überführung.
- 15 9. Eine Waschmittel-Zusammensetzung wie in Anspruch 8 beansprucht, dadurch gekennzeichnet, daß das der Inhibierung der Farbstoff-Überführung fähige Polymere Polyvinylpyrrolidon enthält.
- 20 10. Eine Waschmittel-Zusammensetzung wie in irgendeinem vorstehenden Anspruch beansprucht, dadurch gekennzeichnet, daß sie ein Enzym-System enthält, umfassend zumindest zwei verschiedene Enzyme, ausgewählt aus Proteasen, Lipasen, Amylasen und Cellulasen.
11. Eine Waschmittel-Zusammensetzung wie in irgendeinem vorstehenden Anspruch beansprucht, dadurch gekennzeichnet, daß sie ferner ein Sequestrierungsmittel für zwei- und vielwertige Metalle enthält.
- 25 12. Eine Waschmittel-Zusammensetzung wie in irgendeinem vorstehenden Anspruch beansprucht, welche aus kleinen Teilchen zusammengesetzt ist.

#### Revendications

- 30 1. Composition détergente lessivienne non blanchissante appropriée pour le lavage des textiles délicats, contenant :
  - (a) de 2 à 50 % en masse d'un système tensioactif organique comprenant un ou plusieurs agents tensioactifs anioniques, non ioniques, cationiques, amphotères ou zwitterioniques ;
  - 35 (b) de 0 à 80 % en masse d'un composant édificateur comprenant un ou plusieurs édificateurs de détergence organiques ou inorganiques ;
  - (c) une quantité efficace pour le retrait des tâches d'un polymère de retrait des salissures soluble dans l'eau ou pouvant être dispersé dans l'eau ;
  - 40 (d) de façon optionnelle, d'autres ingrédients détergents, pour atteindre 100 %,
 caractérisée en ce que la composition, en solution aqueuse à 1 % dans de l'eau déminéralisée à 25°C, a un pH ne dépassant pas 10, et en ce que le polymère de retrait des salissures comprend un polyester sulfoné à extrémités non fermées, soluble dans l'eau ou pouvant être dispersé dans l'eau, comprenant des unités monomères de :
  - (i) un monomère diacide aromatique non sulfoné (A),
  - 45 (ii) un monomère diacide aromatique sulfoné (SA),
  - (iii) de façon optionnelle, un monomère diacide aromatique ou aliphatique hydroxylé (HA), dans une quantité remplaçant jusqu'à 50 moles pour cent de (A) ou de (SA),
  - 50 (iv) un polyol (P) sélectionné à partir de l'éthylène glycol, du propylène glycol, de l'isopropylène glycol, du glycérol, du 1,2,4-butanetriol et du 1,2,3-butanetriol, et des oligomères de cela ayant de 1 à 8 unités monomères,
  - 55

le polyester ayant une teneur en soufre comprise dans la gamme allant de 0,5 à 10 % en masse ;

2. Composition détergente selon la revendication 1, caractérisée en ce qu'elle contient de 0,01 à 10 % en masse du polyester (c).
3. Composition détergente selon la revendication 2, caractérisée en ce qu'elle comprend de 0,1 à 5 % en masse du polyester (c).
4. Composition détergente selon l'une des revendications précédentes, caractérisée en ce qu'une solution aqueuse à 1 % en masse de la composition dans de l'eau déminéralisée à 25°C a un pH compris dans la gamme allant de 9,5 à 10.
5. Composition détergente selon l'une des revendications précédentes, caractérisée en ce que le système tensioactif organique contient un sulfate alkyle primaire et/ou un éther sulfate alkyle et/ou un sulfonate d'alkylbenzène, de façon optionnelle en combinaison avec un agent tensioactif non ionique.
6. Composition détergente selon l'une des revendications précédentes, caractérisée en ce qu'elle ne contient pas plus de 0,1 % en masse d'un agent de fluorescence.
7. Composition détergente selon l'une des revendications précédentes, caractérisée en ce qu'elle contient en outre un polymère polycarboxylate sélectionné à partir des polyacrylates et des copolymères acryliques/maléiques.
8. Composition détergente selon l'une des revendications précédentes, caractérisée en ce qu'elle contient en outre un polymère capable d'inhiber le transfert de couleur.
9. Composition détergente selon la revendication 8, caractérisée en ce que le polymère capable d'inhiber le transfert des couleurs comprend de la pyrrolidone de polyvinyle.
10. Composition détergente selon l'une des revendications précédentes, caractérisée en ce qu'elle contient un système d'enzyme comprenant au moins deux enzymes différentes sélectionnées à partir des protéases, des lipases, des amylases et des cellulases.
11. Composition détergente selon l'une des revendications précédentes, caractérisée en ce qu'elle comprend en outre un agent séquestrant des métaux di- et polyvalents.
12. Composition détergente selon l'une des revendications précédentes, caractérisée en ce qu'elle est particulière.

